


Gas-Phase Infrared Spectrum of the Protonated Water Dimer: Molecular Dynamics Simulation and Accuracy of the Potential Energy Surface

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Dedicated to Professor Michele Parrinello on the occasion of his 60th birthday.

The long-awaited observation of the infrared multiphoton dissociation (IRMPD) spectrum of the protonated water dimer

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H_5O_2^+ in the 500–2000 cm^{-1} region (in which the modes of the bridging proton are expected) by Asmis et al.^[1] has raised questions^[2,3] about the assignment^[4] of the observed bands and stimulated more experimental work.^[3,5,6] Most recently, infrared predissociation (IRPD) spectroscopy has been applied to the complex of H_5O_2^+ with Ar,^[5,6] and the spectrum obtained shows some differences to that obtained by IRMPD. Whether these differences are due to the different techniques used, or to perturbation of H_5O_2^+ by Ar in the complex, is presently not clear.

Here we report molecular dynamics (MD) simulations of the vibrational spectra of H_5O_2^+ , its perdeuterated analogue, D_5O_2^+ , and its complex with Ar, $\text{H}_5\text{O}_2^+\cdot\text{Ar}$, on potential energy surfaces (PES) obtained by Møller–Plesset second-order perturbation theory (MP2) with a correlation-consistent basis set (cc-pVTZ) and discuss the accuracy of different potential energy surfaces previously used.

We calculate harmonic vibrational frequencies at the CCSD(T)/cc-pVTZ level using the ACES-II code.^[7] This is the best harmonic result obtained by analytic differentiation published to date. It avoids the unbalanced TZ2P basis set of a previous B-CCSD(T) calculation.^[8] Tables 1 and 2 (see also Supporting Information) compare the results obtained with those of previous calculations. The following observations are made for harmonic frequencies: 1) MP2 is a good approximation. When the same basis set is used CCSD(T) changes the harmonic frequencies by at most 15 cm^{-1} , except for the critical O–H⁺–O asymmetric stretch, which is shifted by 65 cm^{-1} to lower wavenumber. 2) Extending the basis set by diffuse functions for all shells at all atoms (aug-cc-pVTZ basis set) at the MP2 level lowers

the critical O–H⁺–O asymmetric stretch by as much as 77 cm^{-1} , but changes all other frequencies by less than 25 cm^{-1} . 3) Augmentation with diffuse functions on the O atoms only [cc-pVTZ(aug-O)], as motivated by computational savings lowers the O–H⁺–O asymmetric stretch by 57 cm^{-1} . 4) The recent fit^[9] of the CCSD(T)/cc-pVTZ PES (HBB-Fit) yields harmonic frequencies for the O–H⁺–O asymmetric stretch and the terminal OH stretches (ref. [9]; Table 1, last column) that are 35 and 39–44 cm^{-1} , respectively, lower than the present analytic results. 5) The OSS3(p)-Fit^[10] of the MP2/cc-pVTZ(aug-O) PES used for the 4D and VCI calculations^[2] shows frequency deviations from the direct MP2/cc-pVTZ(aug-O) calculation of 47 cm^{-1} for the O–H⁺–O asymmetric stretch, 46 cm^{-1} for the O–H⁺–O_y bend and 110 cm^{-1} for one of the outer H–O–H bends (we refer to the global-minimum data in Table 3 of ref. [11] and Table III of ref. [2]). 6) The TZP (on O), DZP (on H) basis set used in ref. [4] for MP2 calculations yields an O–H⁺–O asymmetric stretching frequency which is 87 cm^{-1} higher than the MP2/cc-pVTZ result (and as much as 158 cm^{-1} higher than the CCSD(T) result), while the O–H⁺–O_{xy} bends are too low by 58 and 48 cm^{-1} (cf. Table I in ref. [4]).

The harmonic approximation is not adequate for strongly hydrogen bonded systems, and in the light of the approximations on the PES we comment on previous quantum calculations that take anharmonicities into account. The quality of the dynamic description depends on the number of degrees of freedom included, on the choice of coordinates and on the treatment of couplings. Normal modes as used in the CC-VSCF^[12] and VCI calculations^[2,11] describe regions outside the reference configuration poorly and become strongly coupled.

For example, the CC-VSCF and VCI models describe the outer symmetric and asymmetric OH stretching vibrations of the two proton-bonded water molecules very poorly (Table 2). The predicted anharmonicities are much too large, and the fundamentals too low. In contrast, second-order perturbation theory (PT),

Table 1. Harmonic vibrational frequencies of the O–H⁺–O bridge^[a].

	CCSD(T) cc-pVTZ	MP2 cc-pVTZ	MP2 aug-cc-pVTZ	MP2 cc-pVTZ(aug-O)	MP2 ref. [4]
symm O–H ⁺ –O stretch	633	631	627	626	628
asymm O–H ⁺ –O stretch	896	961	884	904	1054
O–H ⁺ –O _x bend	1493	1485	1484	1473	1435
O–H ⁺ –O _y bend	1572	1557	1557	1551	1524

[a] See Supporting Information for a complete list of frequencies and intensities.

Table 2. Fundamental frequencies and anharmonic shifts for external H–O–H bends and OH stretches of H_5O_2^+ compared to H_2O [cm^{-1}].

		CCSD(T)	HBB-Fit	MP2/cc-pVTZ	MP2/TZP	OSS3-Fit	Obsd.
		fund (anharmon) this work	DMC fund (anharmon) ref. [22]	PT fund (anharmon) this work	CC-VSCF fund (anharmon) ref. [12]	VCI fund (anharmon) ref. [11]	fund ref. [23]
H_5O_2^+	H–O–H bend, in-phase	1614 ^[a]		1599 (–110)	1662 (–50)	1646 (–70)	
	H–O–H bend, out-of-phase	1895 ^[a]		1889 (+115)	1853 (+50)	1809 (–62)	
	OH symm stretch, out-of-phase	3620 ^[a]	3511(–233)	3613 (–163)	3518 (–291)	3319 (–381)	3609
	OH symm stretch, in-phase	3629 ^[a]	3552(–193)	3622 (–163)	3593 (–224)	3427 (–369)	
	OH assym stretch, out-of-phase	3697 ^[a]	3652(–180)	3701 (–179)	3577 (–343)	3468 (–415)	3684
	OH stretch, in-phase	3696 ^[a]	3652(–180)	3701 (–180)	3579 (–342)	3472 (–422)	3684
H_2O	H–O–H bend	1616(–51)		1600 (–30)	1548 (–67)		1595
	OH symm stretch	3683(–175)		3702 (–169)	3700 (–154)		3657
	OH assym stretch	3775(–189)		3812 (–181)	3798 (–196)		3756

[a] Anharmonic corrections (perturbation theory) taken from MP2/cc-pVTZ calculations.

which uses third- and fourth-order force constants as implemented in the ACES-II code,^[13] explains the observed frequencies in the OH stretching region satisfactorily (Table 2). Diffusion Monte Carlo (DMC) yields virtually identical anharmonicities for the asymmetric OH stretches (Table 2), but larger anharmonicities (and poorer agreement with observed fundamentals) for the symmetric stretches than perturbation theory. This failure of the CC-VSCF and VCI treatments raises doubts about their ability to describe the even more difficult situation in the O-H⁺-O bridge.

The Cartesian coordinates used in (2×2)-dimensional calculations^[4] and also adopted later^[2] for four-dimensional calculations are less coupled and may be better suited than normal modes for the O-H⁺-O bridge. The (2×2)D^[4] and 4D^[2] treatments not only couple the four coordinates of the O-H⁺-O bridge differently, they also differ in how these four coordinates are coupled to the remaining ones of the whole system. While the (2×2) treatment^[4] attempts to take some of this coupling implicitly into account, since the four-dimensional PES is calculated for relaxed (optimized) values of all other coordinates of the system (under the only constraint of fixed mutual orientations of the two water molecules), the 4D calculation of ref. [2] uses a PES which is derived from the full-dimensional fitted PES "by freezing all coordinates outside the O-H⁺-O fragment at their equilibrium values".

In spite of different approximations, the (2×2)D,^[4] CC-VSCF,^[12] 4D^[2] and VCI^[2] models agree in the following for the vibrations of the O-H⁺-O bridge: 1) The splitting between the O-H⁺-O_y and O-H⁺-O_x bends is small (58, 52, 16, 11 cm⁻¹). 2) Compared to the harmonic spectrum the O-H⁺-O asymmetric stretch is shifted up (104, 338, 328, 57 cm⁻¹) and the O-H⁺-O bends are shifted down (467/498, 69/58, 158/161, 117/125 cm⁻¹). 3) The (2×2)D^[4] and 4D^[2] calculations both predict two bands in addition to the fundamentals: an O-H⁺-O symmetric stretching overtone in the region of the O-H⁺-O asymmetric stretch and O-H⁺-O bends, at 1158 and 1120 cm⁻¹, respectively, and a combination of the O-H⁺-O symmetric and asymmetric stretches in the region of the outer H-O-H bends, at 1671 and 1682 cm⁻¹, respectively.

We conclude that the largest uncertainty of the (2×2)D quantum results^[4] comes from the basis set used for calculating the PES. Assuming that this error is largely in the harmonic part, estimates for the O-H⁺-O asymmetric stretching fundamental can be obtained by combining the anharmonic correction from the (2×2)D quantum results^[4] (+104 cm⁻¹) with the MP2/a-ccVTZ harmonic result (884 cm⁻¹). Calculations made with the cc-pVTZ basis set indicate that CCSD(T) may lower the harmonic MP2 value by 65 cm⁻¹. Hence, the O-H⁺-O asymmetric stretch is expected between 923 and 988 cm⁻¹, which supports—as already proposed by Dai et al.^[2]—its assignment to line b of the observed spectrum.

Incidentally, for the present type of symmetric proton-bonded systems, the harmonic MP2/cc-pVTZ result (961 cm⁻¹) seems to be a good predictor for the observed band maximum of the asymmetric O-H⁺-O stretch (921 cm⁻¹), because anharmonic corrections (on the order of +104 cm⁻¹) and changes in the harmonic frequency due to changes of the PES (on the

order of -170 cm⁻¹) partially outweigh each other. Other examples are D₃O₂⁺ with 692 cm⁻¹ (MP2/cc-pVTZ harmonic) versus 697 cm⁻¹ (observed band b')^[1] and the proton-bonded dimethyl ether dimer with 823 cm⁻¹ (MP2/cc-pVTZ, G. von Hellden, personal communication) versus 810 cm⁻¹ observed.^[14]

An alternative method with full coupling and full anharmonicity is the calculation of the IR spectra as the Fourier transform (FT) of the dipole autocorrelation function from trajectories generated by ab initio MD. Its limitation is that quantum

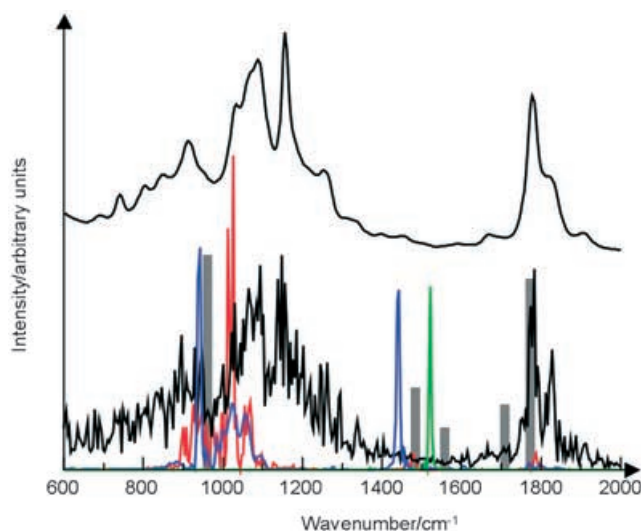


Figure 1. Infrared spectrum of H₅O₂⁺ obtained as Fourier transform of the dipole autocorrelation function. The grey sticks are the harmonic results. The red spectrum was obtained by exciting selectively the asymmetric O-H⁺-O stretching mode, and the blue and green spectra by exciting selectively the O-H⁺-O_{xy} mode. The smoother upper curve is the spectrum obtained by the maximum-entropy method^[24] (200 poles).

effects on the motion of the nuclei are not included. Figure 1 shows results of such a simulation for the MP2/cc-pVTZ PES (Turbomole code,^[15–17] NVE ensemble, time step 0.484 fs, simulation time 4.35 ps, initial velocities randomly chosen at equilibrium structure by assuming a Boltzmann distribution, temperature about 350 K) together with the harmonic stick spectrum. This spectrum is an average over six trajectories. All other spectra are averages over two trajectories that differ only in the direction of the initial velocities. The spectrum is very similar to those previously obtained by MD on MP2^[4] or DFT PES.^[18] Figure 2 shows the same for D₂O₅⁺. The band around 1800 cm⁻¹ (1300 cm⁻¹ for D₂O₅⁺) is due to the H-O-H bends of the two proton-bound H₂O molecules and is unequivocally assigned to band e (e' for D₂O₅⁺). The bands in the region 850–1300 cm⁻¹ (600–950 cm⁻¹ for D₂O₅⁺) correspond to observed bands b–d (b'–d').

Figure 1 also shows spectra obtained from MD trajectories that have been initiated by selective displacements along individual normal modes of the O-H⁺-O unit instead of random velocities. Initial displacements along the O-H⁺-O_{xy} bends (perpendicular to the O-O axis) yield spectra (green and blue curves) with peaks at 1450 and 1520 cm⁻¹, slightly below their harmonic values, shown as grey sticks in Figure 1. This indi-

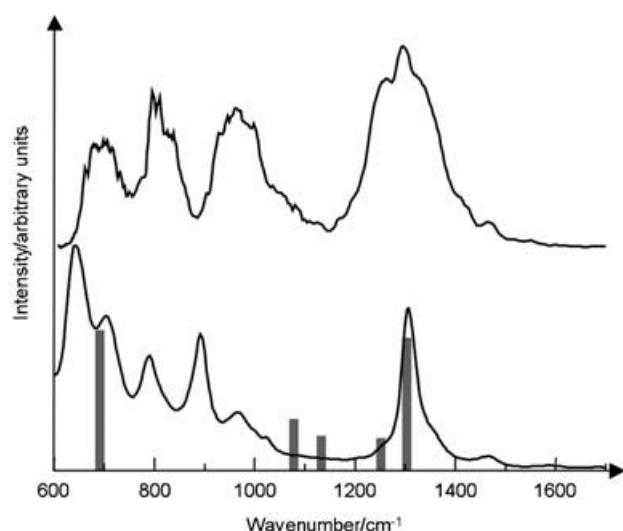


Figure 2. Simulated infrared spectrum of D_5O_2^+ (bottom, harmonic spectrum shown as sticks) compared to the IRMPD spectrum of D_5O_2^+ (top).^[1]

cates a small anharmonic shift to lower wavenumber, which does not change the small splitting seen for the harmonic wavenumbers. The blue curve also has a peak slightly below the harmonic wavenumber of the asymmetric $\text{O}-\text{H}^+-\text{O}$ stretch, which is a result of vibrational energy redistribution. Selective excitation of the asymmetric $\text{O}-\text{H}^+-\text{O}$ stretching mode produces a spectrum (red line) that falls into the broad band between 850 and 1300 cm^{-1} and has a major peak at 1030 cm^{-1} . This implies an anharmonic shift of about $+100\text{ cm}^{-1}$ for the asymmetric $\text{O}-\text{H}^+-\text{O}$ stretch, in qualitative agreement with the quantum dynamic calculations. For the $600\text{--}1000\text{ cm}^{-1}$ band in the simulated D_2O_5^+ spectrum, selective excitation of the asymmetric $\text{O}-\text{D}^+-\text{O}$ stretching mode yields the most intense peak at 750 cm^{-1} , 45 cm^{-1} above the harmonic result.

The intensities of the green and blue lines are at arbitrary scale with the full spectrum. These lines have peaks in the region above 1300 cm^{-1} and below 1650 cm^{-1} (above 950 cm^{-1} and below 1250 cm^{-1} for D_2O_5^+), where the IR spectrum (black line) has very low intensity. The reason is that only modes that involve motions of the bridging proton in the z direction (along the $\text{O}-\text{O}$ axis) change the dipole moment significantly and hence have high intensities (see also ref. [4]). This is further illustrated by Figure 3, which compares the IR spectrum (solid line, FT of the dipole autocorrelation function) with the spectrum obtained as FT of the velocity autocorrelation function of the bridging proton only (dotted and broken lines). Vibrations to which the bridging proton does not contribute should not appear in this spectrum. The intensities do not reflect changes in the dipole moment, but just the vibrational amplitude of the bridging proton. The dotted curve is obtained from the velocity in the z direction, while the dashed curve adds the velocities in x and y directions (perpendicular to the $\text{O}-\text{O}$ axis). The dotted curve virtually reproduces the IR spectrum, which shows that only motions of the bridging proton in the z direction can change the dipole moment of

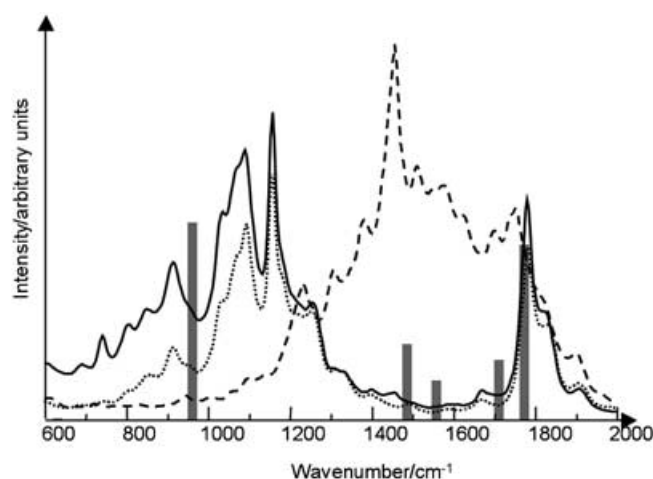


Figure 3. Infrared spectrum of H_5O_2^+ (solid line, harmonic spectrum shown as sticks) and Fourier transform of the autocorrelation function of the velocity of the bridging proton only. Dotted: z component, dashed: $x+y$ components (maximum entropy^[24] with 200 poles applied to all spectra).

H_5O_2^+ to a noticeable extent. The dashed curve has high intensities in the $1300\text{--}1650\text{ cm}^{-1}$ region, where the $\text{O}-\text{H}^+-\text{O}_{xy}$ bending fundamentals have been identified (see Figure 1).

There are two important conclusions from the above analysis: 1) The $\text{O}-\text{H}^+-\text{O}_{xy}$ bends do not contribute to the observed IR spectrum. 2) The broad band between 850 and 1300 cm^{-1} obtains its intensity from motions of the bridging proton in the z direction. Analysis of the MD trajectories shows that these motions cannot be described by the asymmetric $\text{O}-\text{H}^+-\text{O}$ stretching normal mode alone, but are also coupled to low-frequency reorientations of the terminal water molecules (torsion and wagging). This was documented in a previous MD study at the DFT level^[18] and is also in agreement with the recent analysis of a fitted CCSD(T)/aug-cc-pVTZ PES.^[9] These findings show that a low-dimensional quantum treatment which takes only modes of the $\text{O}-\text{H}^+-\text{O}$ unit into account, such as the previous $(2\times 2)\text{D}$ model,^[4] cannot reproduce all features of the broad band between 850 and 1300 cm^{-1} . A recent correlation-function quantum Monte Carlo study^[19] on the OSS3 potential energy surface also identified states with large transition moments arising from couplings of the asymmetric $\text{O}-\text{H}^+-\text{O}$ mode with waggings and torsions of the two water molecules.

Figure 4 shows the simulated IR spectrum of the $\text{H}_5\text{O}_2^+\cdot\text{Ar}$ complex (solid line, bottom). It is virtually identical with the IR spectrum of H_5O_2^+ (dotted line, bottom). In the global minimum structure (Figure 5) Ar binds weakly ($8.5\text{--}11.3\text{ kJ mol}^{-1}$)^[20,21] to H_5O_2^+ in the direction of one of the terminal $\text{O}-\text{H}$ bonds. However, during the MD run it assumes all possible configurations with respect to the central $\text{O}-\text{H}^+-\text{O}$ unit, including all four equivalent $\text{OH}\cdots\text{Ar}$ positions. While the equilibrium structure exhibits a large shift of almost 250 cm^{-1} of the harmonic asymmetric $\text{O}-\text{H}^+-\text{O}$ stretching frequency to higher wavenumbers (see sticks in Figure 4), this effect averages out in the MD simulations.

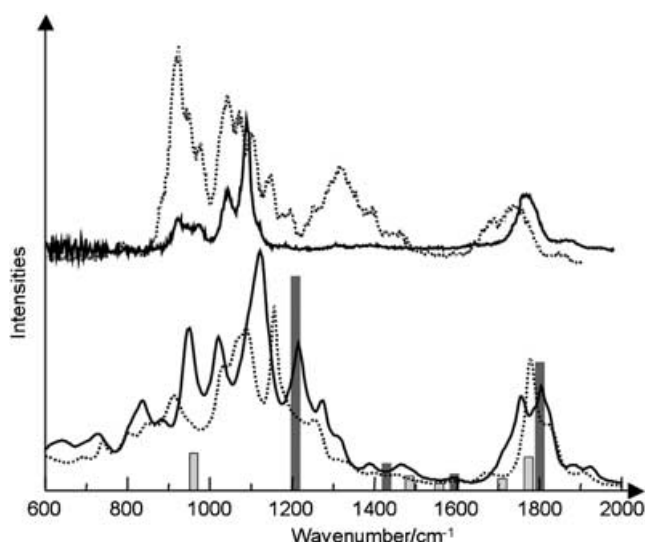


Figure 4. Simulated infrared spectra of H_5O_2^+ (dotted line, bottom) and of the $\text{H}_5\text{O}_2^+\cdot\text{Ar}$ complex (solid line, bottom) with harmonic spectrum shown as sticks, compared to the IRMPD spectrum of H_5O_2^+ (dotted line, top)^[1] and the IRPD spectrum of $\text{H}_5\text{O}_2^+\cdot\text{Ar}$ (black, top).^[6]

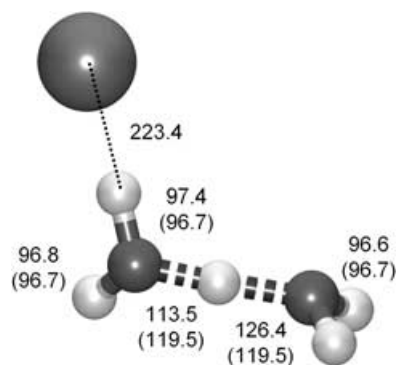


Figure 5. Equilibrium structure of the $\text{H}_5\text{O}_2^+\cdot\text{Ar}$ complex. Bond lengths [pm] and angles [°] in parentheses are for the free H_5O_2^+ ion.

From this comparison we conclude that differences between the IRMPD spectrum^[1] and the IRPD spectrum^[5,6] should be due to the different excitation mechanisms and/or different temperatures.

From the present MD simulations we arrive at the following assignments: The band around 1800 cm^{-1} can safely be assigned to H–O–H bends of the terminal water molecules, the O–H⁺–O_{x,y} bends (perpendicular to the O–O axis) have vanishing IR intensities and should not be seen in the spectra and the bands in the range between 800 and 1300 cm^{-1} are due to motions of the bridging proton in the z direction, which are coupled to torsions and waggings of the terminal water molecules.

Acknowledgements

We thank Knut Asmis, Gert von Helden and Mikhail Vener for discussions and for the privilege to read manuscripts prior to publication.

Keywords: ab initio calculations • hydrogen bonds • IR spectroscopy • molecular dynamics

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Received: February 5, 2005

Published online on July 11, 2005